Development of a MEMS Tool to Study the Physics of Water and Ice

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CNF Project: 2018 Cornell NanoScale Science and Technology Facility Research Experience for Undergraduates Program

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Primary CNF Tools Used: ABM contact aligner, Anatech resist strip, FilMetrics film measurement system, LPCVD nitride furnace, Oxford 81/82 etchers, Oxford PECVD, SÜSS SB8e substrate bonder, SÜSS MA6-BA6 contact aligner, VersaLaser cutting/engraving tool

Abstract:

Freezing of water in confinement is commonly found in geological, biological and architectural contexts. It is believed that the phase equilibrium and crystal formation is influenced by the confinement in pore space, which often has nanoscopic dimensions. The small scale and structural complexity of porous materials hinders our ability to understand the detail kinetics and phase equilibrium of crystals in confinement. To shed light into this problem, we developed a microelectromechanical systems (MEMS) based porous system consisting of geometrically well-defined high aspect ratio nanochannels with nanoscale (30 nm to 100 nm) channel heights and micron-scale channel width. Such configurations provide a wide field of view (~microns) for direct visualization of crystallization kinetics and phase equilibrium within nanoconfinement. Channels were first fabricated via conventional photolithography techniques on silicon and glass substrates. Notably, a 200 nm silicon nitride layer was deposited via low pressure chemical vapor deposition (LPCVD) underneath the channels to enhance contrast between liquid water and ice. The final channel geometries were verified via capillary condensation within the channels. Finally, we experimentally observed the ice-water interface in nanoconfinement. The melting of confined ice is in quantitative agreement with the Gibb-Thomson relation.

Project Summary:

Introduction. Freezing of water in nanoconfinement is of great importance in geological, biological, and archeological contexts [1,2]. It is believed that the phase equilibrium of water and ice is shifted according to the Gibbs-Thomson relation [3] (Figure 1). However, owing to the small and complex geometrical nature of porous materials, the local phase equilibrium in nanoconfinement remains unresolved. Direct imaging of freezing can provide local mechanistic information on water-ice phase equilibrium and crystallization dynamics under confinement. Herein, we demonstrate the unique opportunity of observing confined phase equilibrium in a MEMS high aspect ratio nanochannel array with *in situ* phase contrast enhancement enabled by a silicon nitride (Si_3N_4) dielectric mirror [4] (Figure 2).

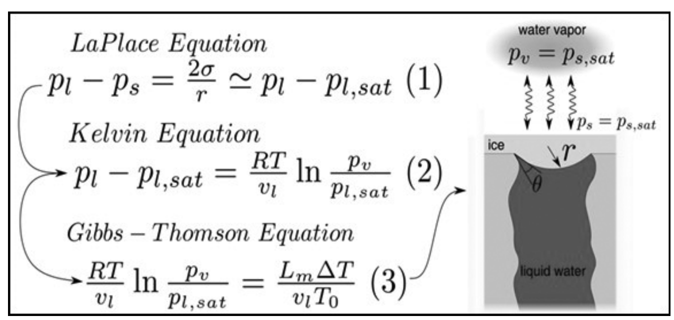

Figure 1: Liquid water in a pore can coexist, metastably, with ice and an unsaturated vapor. Capillarity between liquid and ice (Laplace) places the liquid under tension and allows for phase equilibrium (Kelvin) with the liquid under tension. This equilibrium can be expressed as the Gibbs-Thomson equation.

Fabrication and Experiment. The device fabrication process can be summarized as follows: A LPCVD Si_3N_4 layer of ~ 200 nm thickness was first deposited on a silicon wafer followed by a PECVD layer of silicon oxide with thickness corresponding to the desired channel height. Nanochannel patterns were then transferred and patterned via photolithography. The channels were formed by etching the oxide layer with 30:1 buffered oxide etch (BOE).

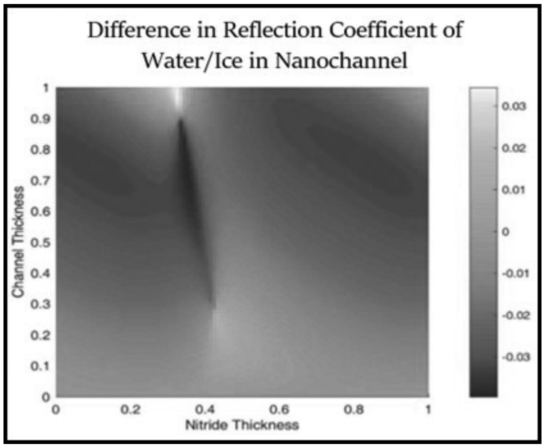

Figure 2: Calculated difference in the reflection coefficient of water and ice in the nanochannels, with axes normalized to incident wavelength. The maximum difference is found with nitride thickness in between 0.4 and 0.5, which for visible light correlates to a nitride thickness of 130 nm-260 nm. This difference is insensitive to channel thickness.

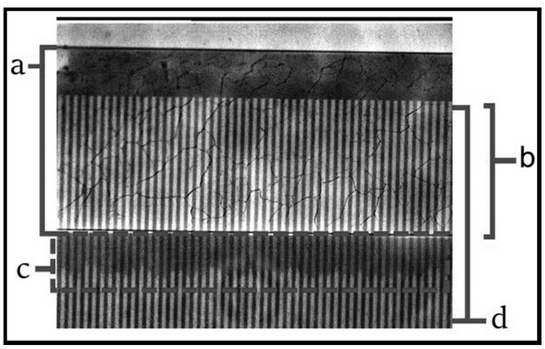

Figure 3, top: Image obtained from freezing experiment. (a) Microchannel containing bulk ice, identified by the grain boundaries present in image. (b) 500 µm channel overlap. (c) Liquid water in nanochannels (darker region) coexisting with ice (brighter region) at subfreezing temperature. (d) Nanochannel array.

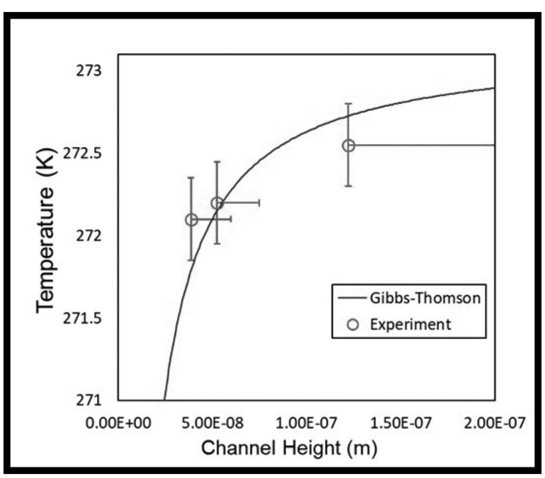

Figure 4, bottom: Melting temperatures of ice in nanochannels with different channel heights compared to the Gibbs-Thomson prediction. Values agree with those predicted by the Gibbs-Thomson relation.

For the glass wafer, a 250 nm PECVD amorphous silicon (α-Si) layer was deposited and annealed as an etch mask. Photolithography was then used to transfer the pattern of microchannels. SF_6/O_2 reactive ion etch in the Oxford 80 etcher was used to pattern the α-Si etch mask and the 10 µm microchannels were etched in 49% hydrofluoric acid.

When complete, the patterned silicon and glass wafers were aligned and anodically bonded using the MA6-BA6 contact aligner and SÜSS SB8e substrate bonder. The bonded wafers were diced and microchannel inlets were cut out with the VersaLaser.

For testing, individual devices were placed in an environmental chamber with pressure and temperature regulation. Water vapor was then pumped through the chamber to fill the nanochannels with liquid water upon capillary condensation, from which the channel height was deduced. The microchannels were filled by condensation by further raising the vapor pressure to saturation. Once filled, the chamber temperature was lowered to initiate freezing in the nanochannels and confined phase equilibrium was captured with a CCD camera positioned above the chamber. The nanoconfined water-ice phase equilibrium was successfully captured as shown in Figure 3. The melting temperatures of confined ice were reported in Figure 4 and were consistent with the Gibbs-Thomson prediction.

Conclusions:

A microfluidic device consisting of high aspect ratio nanochannels was fabricated. A layer of ~ 200 nm Si_3N_4 was deposited underneath the channels, resulting in detectable contrast between the liquid water and ice in the channels. The melting temperatures of confined ice agreed with the Gibbs-Thomson relation. Continued work will focus on studying the transport dynamics of ice-water in confinement.

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